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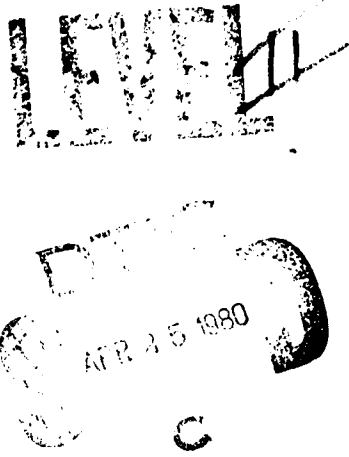
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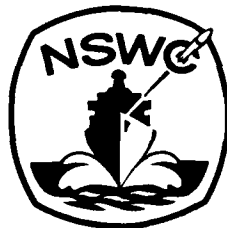
## THE PHOTOLYSIS OF FLUOROTRINITROMETHANE

BY DOROTHY A. CICHRA

RESEARCH AND TECHNOLOGY DEPARTMENT

21 JANUARY 1980

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| 4. TITLE (and Subtitle)<br>The Photolysis of Fluorotrinitromethane  |                                      | 5. TYPE OF REPORT & PERIOD COVERED<br>Preliminary Report   |
| 7. AUTHOR(s)<br>Dorothy A. Cichra   |                                      | 6. PERFORMING ORG. REPORT NUMBER   |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Naval Surface Weapons Center<br>White Oak<br>Silver Spring, Maryland 20910   |                                      | 10. PROGRAM ELEMENT PROJECT TASK<br>AREA & WORK UNIT NUMBERS<br>61152N; ZR00001<br>ZR01309; R01201 |
| 11. CONTROLLING OFFICE NAME AND ADDRESS   |                                      | 12. REPORT DATE<br>21 January 1980   |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)   |                                      | 13. NUMBER OF PAGES<br>13  |
|   |                                      | 15. SECURITY CLASS. (of this report)<br>Unclassified   |
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| 18. SUPPLEMENTARY NOTES   |                                      |  |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number)<br>Photolysis<br>Fluorotrinitromethane<br>Fluorodinitromethane   |                                      |  |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>The photolysis of fluorotrinitromethane was studied as a possible route to fluorodinitromethane. The photolysis in hydroxylic solvents gives fluorodinitromethane in yields (non-isolated) ranging from 25-50% under non-optimized conditions. Fluorodinitromethane appears not to be formed in the photolysis in non-hydroxylic solvents. |                                      |  |

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SUMMARY

Fluorodinitromethane is a key intermediate in the synthesis of several energetic plasticizers containing the fluorodinitromethyl group as energetic moiety. This report describes the basis of a new synthesis for this compound which has significant advantages over existing methods. The work was carried out under the NAVSWC Independant Research Program, Task IR-201.

*J. W. Enig*

J. W. ENIG  
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CONTENTS

|                                | Page |
|--------------------------------|------|
| I INTRODUCTION.....            | 3    |
| II RESULTS AND DISCUSSION..... | 3    |
| III EXPERIMENTAL.....          | 5    |

## I. INTRODUCTION

There is little work on the photolysis of fluorotrinitromethane reported in the literature. A flash photolysis study<sup>1</sup> indicated that under some conditions the photolysis of fluorotrinitromethane results in the formation of fluorodinitromethyl anion. It is reported<sup>1</sup> that on flash photolysis in absolute methanol an absorption with  $\lambda_{\text{max}}$  of about 375 nm appears, quickly reaching a maximum, and then decaying. This absorption was attributed to the fluorodinitromethyl anion. The maximum absorbance observed is reported to correspond to a yield of fluorodinitromethyl anion of about 1%. On the addition of sodium methoxide to the photolyzed solution, an absorbance corresponding to a yield of fluorodinitromethyl anion of 11% was observed.

In a mixture of methanol and toluene, on the addition of sodium methoxide to the photolyzed solution, a yield of 3% of fluorodinitromethyl anion was observed<sup>1</sup>. In acetonitrile no fluorodinitromethyl anion was observed<sup>1</sup> and no decrease in the amount of fluorotrinitromethane was apparent.

Because of the reported<sup>1</sup> formation of the fluorodinitromethyl anion in the flash photolysis, we decided to investigate the photolysis of fluorotrinitromethane further to determine if it had any use as an alternate synthetic route to fluorodinitromethane.

## II. RESULTS AND DISCUSSION

The flash photolysis<sup>1</sup> of fluorotrinitromethane in hydroxylic solvents is reported to result in decomposition of the fluorotrinitromethane (to an extent of 10-20%) to give an intermediate which was identified as the fluorodinitromethyl anion (in yields up to 10-15%). The results obtained in the present study are consistent with the earlier observations. When fluorotrinitromethane is irradiated continuously with an unfiltered medium pressure mercury arc lamp in a hydroxylic solvent, it readily decomposes, resulting in the formation of fluorodinitromethane (as identified by gas chromatography and ultraviolet spectroscopy).

<sup>1</sup>Balykin, V. P. and Slovetskii, V.I., "The Photochemistry of Aliphatic Nitro Compounds 3. Flash Photolysis of Fluorotrinitromethane Solutions" Izv. Akad. Nauk. SSSR, Ser. Khim., No. 9, 1976, p. 1970.

Photolysis of fluorotrinitromethane in methanol results in the formation of fluorodinitromethane in 20-30% yield. Changing the solvent to iso-propanol increases the yield while having little, if any, effect on the rate of the photolysis. Photolysis in iso-propanol results in the formation of fluorodinitromethane in about 50% yield.

The yield of the fluorodinitromethane in methanol can also be increased by the addition of acid to the solution to be photolyzed. Thus, photolysis of fluorotrinitromethane in methanol containing sulfuric acid (where the acid concentration is about four times that of the fluorotrinitromethane) results in the formation of fluorodinitromethane in about 50% yield.

The photolysis in methanol was also carried out using pyrex filtered light. While the photolysis is slower in this case, the yield appears to be the same as with the unfiltered light.

The fluorodinitromethane appears to be the major product in the above photolysis. Although there appear to be other products formed, no attempt was made to analyze the reaction mixture completely. Neither were any attempts made at optimizing the yield of the fluorodinitromethane or of isolating it.

The flash photolysis study<sup>1</sup> of fluorotrinitromethane indicated that in non-hydroxylic solvents decomposition of the fluorotrinitromethane did not occur. No decrease in the fluorotrinitromethane was observed in acetonitrile, and no intermediates were detected. The present study revealed that, on continuous photolysis in non-hydroxylic solvents, fluorotrinitromethane does decompose; however, the decomposition occurs at a much slower rate than in hydroxylic solvents. Only trace amounts, if any, of fluorodinitromethane is formed in these photolyses however.

Photolysis of fluorotrinitromethane in methylene chloride with unfiltered light for a time sufficient to completely decompose it in a hydroxylic solvent resulted in only about 20% decomposition of the fluorotrinitromethane. The major new components in the photolysis mixture, observed by gas chromatography, were chloroform and a product that appears to be fluorochlorodinitromethane. (It has the same gas chromatographic retention time as the product obtained by the reaction of fluorodinitromethane with chlorox. The product from the reaction of fluorodinitromethane and chlorox has an infrared spectrum consistent with that reported<sup>2</sup> for chlorofluorodinitromethane.) The origin of the chloroform is unknown; however, photolysis for similar time periods of methylene chloride not containing fluorotrinitromethane did not lead to formation of chloroform.

<sup>2</sup>Okhlobystina, L. V., et al. "Fluorination of Salts of Polynitrohydrocarbons with Perchloryl Fluoride," Izv. Akad. Nauk. SSSR, Ser. Khim., No. 7, 1971, p. 1,487.

Photolysis in acetonitrile for similar time periods again results in about a 20% decomposition of the fluorotrinitromethane. In this case, no new components were detected in the photolysis mixture by gas chromatography under the conditions used to analyze the other photolyses.

Because of the much slower rate of photolysis in these non-hydroxylic solvents and the apparent lack of formation of fluorodinitromethane, these photolyses were not investigated further.

### III. EXPERIMENTAL

General. The photolyses were carried out using a medium pressure mercury arc lamp placed in a quartz cooling well. The solutions to be photolyzed were placed in quartz tubes which were then positioned around the outside of the cooling well at distances of about 3 to 4 inches from the cooling well.

The photolyzed mixtures were analyzed for products on both a 5 ft. 1/4 inch 10% fluorosilicone column and a 6 ft. 1/8 inch 10% UCCW 982 column. Products were identified by comparison to authentic material. However to minimize interference from the solvent, quantitative results were obtained for the photolyses in the hydroxylic solvents on only the fluorosilicone column at 80°C, while those for the photolyses in non-hydroxylic solvents were obtained on the UCCW 982 column at ambient temperature.

The photolyses in hydroxylic solvents were also analyzed by ultraviolet spectroscopy. (The method used was similar to that for analysis of fluorodinitromethanol<sup>3</sup>). The photolyzed mixture was diluted with water (50  $\mu$ L photolysis mixture to 10 mL water). The resulting aqueous solution was then added to 0.01M sodium hydroxide (30  $\mu$ L aqueous solution to 10 mL sodium hydroxide). The resulting solution was then analyzed immediately at 382 nm. The concentration (moles/liter) was calculated as the observed absorbance/19,400 for a 1 cm cell.

The photolyses were generally followed by gas chromatography, and were stopped when most of the fluorotrinitromethane had decomposed to prevent further photolysis of any initially formed products.

<sup>3</sup> Glover, D. J., Personal Communication.



PHOTOLYSIS OF FLUOROTRINITROMETHANE IN METHANOL. Fluorotrinitromethane (350  $\mu$ l) was dissolved in methanol (5 ml), then 3 ml of the solution was placed in a quartz tube and photolyzed for 8.5 hrs. Gas chromatography on the final solution revealed the presence of fluorodinitromethane and two other small peaks of retention time similar to that of fluorotrinitromethane. All the fluorotrinitromethane had decomposed. Analysis by uv spectroscopy indicated that the yield of fluorodinitromethane was 28%.

A photolysis of a similar solution in a pyrex tube for 7.5 hrs. resulted in about 80% reaction of the fluorotrinitromethane and formation of fluorodinitromethane in 22% yield (a 26% conversion). The same two other peaks present in the photolysis in quartz were present also.

PHOTOLYSIS IN METHANOL WITH SULFURIC ACID. Methanol was added to 350  $\mu$ l of sulfuric acid to make 5 ml. To this was added 350  $\mu$ l of fluorotrinitromethane. then 3 ml of this solution was photolyzed in a quartz tube for 7.5 hrs. Gas chromatographic analysis indicated that about 96% of the fluorotrinitromethane had decomposed. The mixture contained fluorodinitromethane and the same two other products as in the photolysis in plain methanol. The yield of fluorodinitromethane was 51% by uv spectroscopy.

PHOTOLYSIS OF FLUOROTRINITROMETHANE IN ISOPROPANOL. Fluorotrinitromethane (350  $\mu$ l) was dissolved in 5 ml of isopropanol, then 3 ml of the resulting solution was photolyzed in a quartz tube for 5.75 hrs. No fluorotrinitromethane remained, and analysis by gas chromatography revealed the presence of fluorodinitromethane and one other peak of retention time slightly shorter than fluorotrinitromethane. Analysis of the mixture by uv spectroscopy indicated that the yield of fluorodinitromethane was 53%.

PHOTOLYSIS OF FLUOROTRINITROMETHANE IN METHYLENE CHLORIDE. Fluorotrinitromethane (100  $\mu$ l) was dissolved in methylene chloride (5 ml), then 3 ml of the solution was photolyzed in a quartz tube for 5.5 hrs. Gas chromatography indicated that 80% of the fluorotrinitromethane remained. Two other peaks were present, one was chloroform, the other appeared to be fluorochlorotrinitromethane.

PHOTOLYSIS OF FLUOROTRINITROMETHANE IN ACETONITRILE. Fluorotrinitromethane (100  $\mu$ l) was dissolved in 5 ml of acetonitrile, then 3 ml of the solution was photolyzed for 5.5 hrs. Gas chromatography indicated that 80% of the fluorotrinitromethane remained. No other peaks were apparent.

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